Anais do
60º Congresso Brasileiro do Concreto
CBC2018
Setembro / 2018

@ 2018 - IBRACON - ISSN 2175-8182

The effect of superabsorbent polymers on the cracking behavior due to autogenous shrinkage of cement-based materials

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Abstract

As far as durability is concerned most of the deteriorating mechanisms acting on concrete structures are related to the ingress of aggressive agents inside the structures. Reinforcement corrosion, carbonation and problems during freeze-thaw cycles are related to the ingress of substances such as chlorides, sulfates, carbon dioxide and even water, amongst others. Even before reaching its hardened state, a cement-based composite is subjected to the formation of cracks especially due to the effects of shrinkage during the early ages. The formed porosity of the material can become the perfect path for the ingress of those aggressive agents. The shrinkage phenomena, especially when referred to autogenous and plastic shrinkage are inherent to the hydration process of the cementitious material and (among other factors) are a function of the water-to-cement ratio and curing conditions (temperature and humidity). The use of superabsorbent polymers has proven to be an interesting alternative in the mitigation of shrinkage and reducing shrinkage cracking by means of internal curing. They can also promote sealing and autogenous healing. In this study, different cement pastes and mortars were produced with different combinations of superabsorbent polymers. Their effects on the shrinkage cracking behavior was studied. Both polymers used have already been (individually) studied in previous research and results showed different benefits regarding the crack mitigation and self-sealing and -healing of the samples. In this paper different combinations of those polymers were studied aiming to achieve a composition with optimal properties for the mitigation of autogenous shrinkage. The experimental program of the study was based on the monitoring of autogenous strain and the effect of the polymers in the properties of specimens in the fresh and hardened state. To accomplish that, the hydration and setting time of the mixtures were evaluated by means of ultrasonic measurements (p-wave); the autogenous strain was measured from the final setting time till the age of 7 days following the method described in the ASTM C-1698-09 and mechanical strength tests were also performed.
keywords: superabsorbent polymers, hydrogel, shrinkage, healing, durability.

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1 Problem statement

Most of the deteriorating mechanisms acting on concrete structures are related to the ingress of aggressive agents inside the structures. Even before reaching its hardened state, a cement-based composite is subjected to the formation of cracks especially due to the effects of shrinkage during the early ages. The formed porosity of the material can become the perfect path for the ingress of those aggressive agents. After the crack formation the water intrusion cause a drop in the pH of the concrete that can lead to steel corrosion; the ingress of chlorides causes the de-passivation of the protective film, the intrusion of CO_2 can cause carbonation and both processes can accelerate the corrosion.

The shrinkage phenomena, especially when referred to autogenous and plastic shrinkage are inherent to the hydration process of the cementitious material and (among other factors) are a function of the water-to-cement ratio and curing conditions (temperature and humidity). The autogenous shrinkage is related to the self-desiccation initiated in the pores of the material due to the hydration process (SAHINAGIC-ISOVIC et. al, 2012).

The crack formation due to autogenous shrinkage can be avoided by different means, and an interesting one is the incorporation of superabsorbent polymers (JENSEN; HANSEN, 2001).

Superabsorbent polymers (or hydrogels) are a natural or synthetic water-insoluble 3D network of polymeric chains cross-linked by chemical or physical bonding. They possess the ability to take up a significant amount of fluids from the environment (in amounts up to 500 times their own weight). The swelling and posterior water release are of great interest in the study of smart self-healing materials but can also be explored to promote self-sealing (MIGNON et al., 2017; SNOECK, 2015; MECHTCHERINE et al., 2009; JENSEN, 2008).

In this study, different cement pastes and mortars were produced with different combinations of superabsorbent polymers. Their effects on the shrinkage cracking behavior was studied. Both polymers used have already been (individually) studied in previous research and results showed different benefits regarding the crack mitigation and self-sealing and -healing of the samples. In this paper different combinations of those polymers were studied aiming to achieve a composition with optimal properties for the mitigation of autogenous shrinkage and future applications for self-sealing.

2 Experimental program and discussion of results

In this section information is provided about the materials, compositions of the cement pastes and mortars, mixing procedures, the tests performed and the results.

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2.1 Pastes

The cement pastes were produced with cement CEM I 52.5N in compliance with the standard EN 197-1 (CEN, 2011), a polycarboxylate-type of superplasticizer (Glenium 51 35% conc., BASF, Germany), and two different types of superabsorbent polymers henceforth referred to as SAP1 and SAP2 (for more information please refer to Table 1).

Table 1 – Characteristics of the SAPs (SNOECK, 2015; PELTO et al., 2017)

Name	Type	Production method	Size (µm)	Absorption capacity (g/g SAP)	
				Demineralized water	Cement filtrate solution
SAP 1	copolymer of acrylamide - sodium acrylate	Bulk/BASF, Germany	100 ± 22	305 ± 4	61 ± 1
SAP 2	cross-linked acrylate copolymer	Bulk/SNF Floerger, France	362 ± 19	322 ± 6	47 ± 2

The mixing procedure adopted for all the mixtures followed the standard NBN EN 196-1 (CEN, 2016), as follows:

1. Cement and water mixed for 60 s with low speed (140 rpm);
2. Mixing for 30 s at high speed (285 rpm);
3. Resting of the mixture for 90 s (with scraping of mortar from the surface of the mixing bowl during the first 30 s of the pause);
4. Final mixing during 60 s at high speed (285 rpm).

In the mixtures containing SAPs, the SAP particles were initially dry-mixed with the cement for 30 s at low speed (140 rpm) to ensure a homogenous distribution within the cement. The superplasticizer was added with the water and the mixer was kept working during the step-2 mentioned above.

The hardening and autogenous shrinkage of specimens with and without SAPs were studied. Initially two reference mixtures were produced with a water-to-cement ratio (w/c) of 0.30 and 0.354, following the theory proposed by Powers and Brownyard (1948) and Jensen and Hansen (2001). This low w/c was chosen to highlight the effects of the autogenous shrinkage. The amount of superplasticizer was taken constant at 0.42 m% (of the cement weight).

The dosage of superabsorbent polymers was determined based on the workability of the mixtures. The amount of SAP was determined that could be added to the mixture with a total w/c of 0.354 and showing the same workability as the reference mixture with a w/c of 0.30, based on the assumption that the polymers would absorb the difference in w/c ratio (0.054). The final mixture thus has an effective water content equal to the reference (w/c of 0.30).

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For both pastes and mortars the SAPs were used individually and in combination with the proportion of 30% of SAP1 and 70% of SAP2 (henceforth referred to as SAP1+2). This proportion with more SAP2 was chosen considering that the polymer with larger diameter would be better for the self-sealing and self-healing of cracks to be studied in the future (SNOECK et al., 2012 & 2014a). Combining the features of both materials could lead to the achievement of a mixture with the ability of self-healing and self-sealing.

The workability was assessed by means of the flow table test, according to the standard EN 1015-3 (CEN, 1999). It was found that for SAP1 an amount of 0.11 m% over the mass of cement was needed to absorb the amount of water corresponding to the additional 0.054 water to cement ratio (resulting in an absorption capacity of 51.06 g/g). For SAP2 that amount was corresponding to 0.25 m% over the cement mass (resulting in an absorption capacity of 22.03 g/g). Both values are inferior to the ones shown in Table 1, but it is important to highlight that the values in Table 1 are only a reference for an initial estimation of the dosage of the polymers. The composition of the cement filtrate may differ from the real pore solution of the mixtures (concerning the concentration of ions, especially) (SCHRÖFL et al, 2017).

The determination of setting time of the pastes was made by an automatic Vicat apparatus according to EN 196-3 (CEN, 2005).

The hardening of the pastes was also studied by measuring the ultrasonic wave velocity through a specimen. The equipment used was the FreshCon system (Figure 1). In this system an electric pulse is sent from the computer through the amplifier to the piezoelectric transmitter generating the ultrasonic wave (compressive wave). The waves thus go from one transducer to the other through the specimen and the velocity of the wave propagation is recorded. The measurements were automatically performed each five minutes during 48 hours with a amplifying voltage of 450 V.

Figure 1 - FreshCon equipment

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The setting times (initial and final) can be determined by observing the inflection points of the curves obtained from the measurements (TRTNIK et al., 2008; ROBEYST et al., 2008). The points were taken from the maximum and minimum values of the first derivative of the polynomial function that best fitted the curves. After the initial setting the mixture loses its workability and plasticity which represents a positive increase in the wave velocity through the specimen. With the final setting the mixture becomes rigid and solid. With no more big changes in the structure of the material the wave velocity tends to reach constant values, which is characterized by the decrease in the velocity rate of the curve.

Table 2 shows the results of the setting times determined with both methods. Figure 2 shows the curves obtained with the FreshCon system. Both methods showed a good correlation for the results of the final setting. The values obtained with the FreshCon system are slightly later than those obtained with the Vicat apparatus which could be explained by the fact that the specimens in the first one remain covered during the whole time (a boundary condition for autogenous shrinkage testing), which can prevent the loss of water by evaporation (which does not happen in the latter). In an overall analysis, the addition of SAPs did not provoke big changes in the final setting time (as for the results of the Vicat apparatus).

Table 2 – Setting times of the mixtures

Mixture	Initial setting time (h)		Final setting time (h)	
	Vicat apparatus	FreshCon system	Vicat apparatus	FreshCon system
REF0.30	5.93	5.47	13.0	13.66
REF0.354	7.50	6.33	13.25	14.98
SAP1-0.11%	4.33	4.48	11.75	16.43
SAP2-0.25%	4.50	6.20	13	15.15

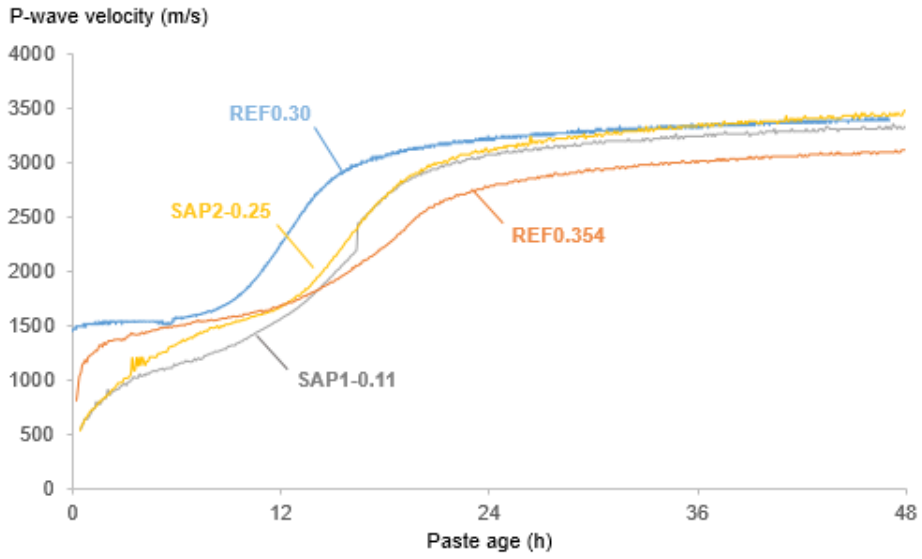

Figure 2 - Velocity graph of the mixtures

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Despite the limited noise in the measurements of the wave velocity (which could cause some distortions in the position of the inflection points and resulted in a few unexpected values for the setting time) it still possible to make some observations.

The wave velocity at the late ages of the specimens is almost the same for the reference mixture and the ones with the SAPs. On the other hand, the velocity at the same ages for the mixture with w/c 0.354 is considerably lower. This could indicate the difference in the porosity of the specimens after setting, considering the additional water content in the REF0.354. In that sense one could assume that the amount of SAPs used in the paste specimens (0.11% SAP1 and 0.25% SAP2) did not promote a large increase in the total porosity as the macro-pores are filled with the swollen SAP particles.

The autogenous shrinkage was assessed according the standard C1698-09 (ASTM, 2009). The test consists of the measurement of the deformation of specimens in corrugated tubes with a nominal length of 425±5 mm and a diameter of 29±0.5 mm. The specimens were placed on metallic supports with one linear variable differential transducer (LVDT) with a range of 5 mm on one end (Figure 3). The measurements were performed continuously every 10 minutes for 7 days in a room with controlled humidity (60±5%) and temperature (20±1°C).

Figure 3 - Set up for the autogenous shrinkage measurement (LVDT's on the bottom of the image)

The zero point for the measurements was considered as the final setting time previously determined. The values obtained with the Vicat method were the ones used. The autogenous strain at a time t (in μm/m) was determined according to Equation 1.

$$\frac{R(t)-R(t_{fs})}{L(t_{fs})} \cdot 10^6 \qquad \text{(Equation 1)}$$

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where R(t) stands for the reading of the LVDT (mm) at time t; R(t_{fs}) for the reading at the moment of final setting; L(t_{fs}) for the length of the tube at the time of final setting. The results for all the measurements are shown in Figure 4.

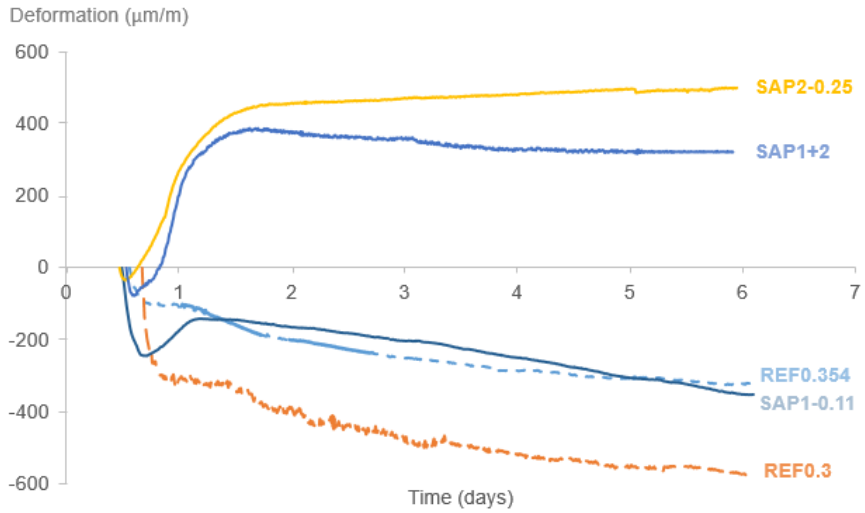

Figure 4 – Deformation due to autogenous shrinkage of the specimens

As expected, the reference mixture REF0.30 presented the higher deformation and shrinkage during the whole period of testing. The mixture REF0.354 showed a slightly smaller deformation over the whole time due the higher amount of water in the mix.

For the mixtures with the SAPs one can verify that the mixture produced with SAP1 presented a smaller deformation in comparison with REF0.3 but still no mitigation of the autogenous shrinkage. On the other hand, the mixture with SAP2 presented a small shrinkage deformation a few minutes after the final setting followed by a remarkable expansion that remained constant from the second to the sixth day of measurements, mitigating all the shrinkage during that period. With almost the same behavior, the mixture produced with the combination of SAP1 and SAP2 also showed a complete mitigation of the autogenous shrinkage from some minutes after the final setting until the sixth day of measurements, presenting a smaller expansion in comparison with the mixture with only SAP2 and a slight reduction in the expansion that became constant around the fourth day of testing.

Even though the same amount of additional water has been used in all the mixtures with the goal of reducing/mitigating the autogenous shrinkage, the fact that the mixture with SAP1 did not show the expected behavior raises evidence that the polymer might not be releasing the water at the ideal time, although literature has shown the ideal release of water by this SAP to mitigate shrinkage (SNOECK et al., 2017). The absorption has been verified with the changes in the workability of the pastes (and mortars as it will be shown in the next section) and this specimen presented almost the same behavior as the REF0.354. Furthermore, the

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fact that the mixture with the combination of SAPs presented smaller values of expansion and a slight reduction of this behavior at some point also sustains this assumption. In literature, the total SAP1 amount used is double, due to a difference in flow value testing (SNOECK et al., 2015). Future research will focus on the evaluation of the absorption of water by SAP1 by an in-depth analysis of the experimental program.

2.2 Mortars

The mortars were also produced with cement CEM I 52,5N following the guidelines of the standard mentioned before, silica sand 0/2, SAP1 and SAP2.

Mortars were used to evaluate the influence of the superabsorbent polymers on the mechanical strength of the specimens at the ages of 2, 7 and 28 days. The compressive and flexural strength were measured on prismatic specimens with dimensions 40 x 40 x 160 mm³ according to the standard EN 196-1 (CEN, 2016). The mixtures were produced with a w/c of 0.50. In this case the dosage of polymers used was 0.5 m% (over the mass of cement) and the amount of additional water needed for the mixture to present the same workability as the reference was determined (Figure 5).

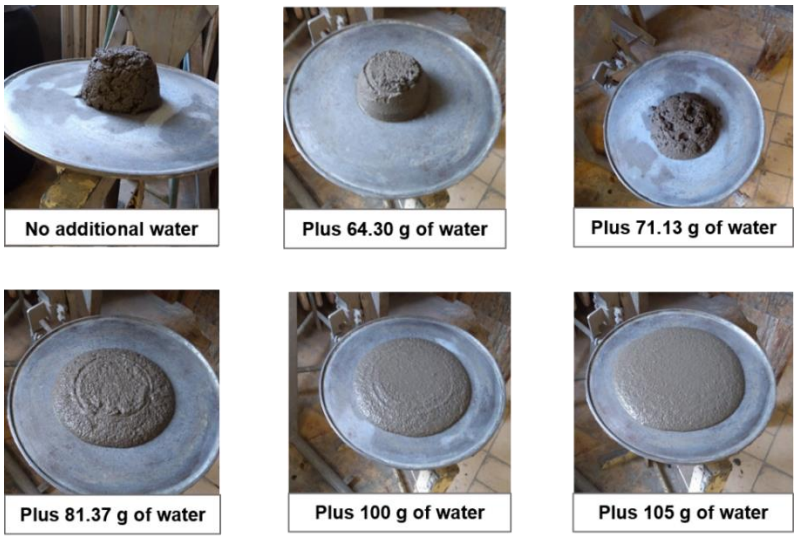

Figure 5 – Changes in the workability of the mortar SAP1-0.5 with the different amounts of additional water; the consistency shown on the bottom right figure is the same as for the REF

The mixing procedure adopted was similar to the one used in the pastes, as follows:

1. Cement and water mixed for 30 s with low speed (140 rpm);
2. Addition of sand during 30 s with the mixer working at low speed (140 rpm);
3. Mixing for 30 s at high speed (285 rpm);
4. Resting of the mixture for 90 s (with scraping of mortar from the surface of the mixing bowl during the first 30 s of the pause);

5. Final mixing during 60 s at high speed (285 rpm).

Figure 6 and Figure 7 show the results for the compressive and flexural strength, respectively, for the mixtures containing SAPs (dosage of 0.50%) as well as the reference at the ages of 2, 7 and 28 days.

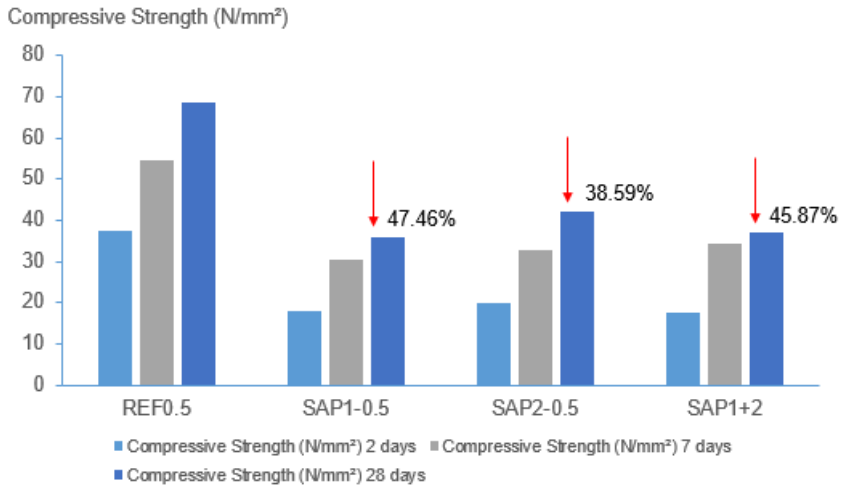

Figure 6 – Compressive strength of the specimens

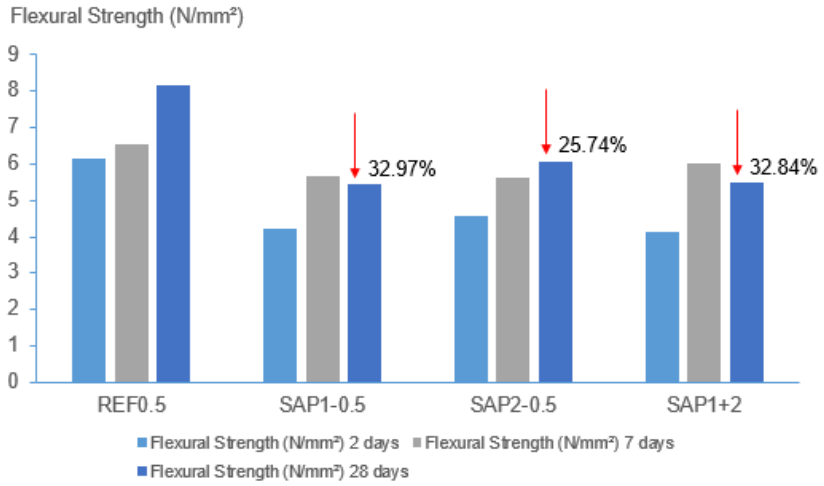

Figure 7 - Flexural strength of the specimens

As it can be seen, all the mixtures containing SAPs presented a reduction in the mechanical strength (both compressive and flexural). This can be associated to the fact of the increase in the porosity of the specimens due to the formation of macro-pores after the SAPs release the absorbed water and the particle returns to the original size (SNOECK et al., 2014). Tests were also performed at an age of 28 days with a dosage of 1.0 m% of SAP1 and SAP2 and

the reduction in strength reached 72% for SAP1 and 57% for SAP2. Snoeck et al. (2014a) have found the dosages of 0.5 m% and 1.0 m% to be more effective for self-healing and self-sealing of mortar specimens, however, as it was seen in the previous section, lower dosage of SAPs were found sufficient for mitigation of autogenous shrinkage alone and are expected to result in a lower mechanical strength loss.

Comparing both types of SAPs one can verify that the mixtures with SAP1 presented the larger reduction in the mechanical strength compared to the ones containing SAP2 and the composition SAP1+2. As explained by Snoeck et al. (2014) this behavior can be associated with the difference in the particle size and absorption capacity of the SAPs (with SAP1 being smaller having a higher absorption capacity in cement filtrate and in the paste, as shown in section 2.1).

3 Conclusions

Cracking in concrete has been for long an issue quite difficult to mitigate. Drying, thermal, chemical, plastic and autogenous shrinkage all happen in different stages of the structure ‘s life, under certain boundary conditions, which makes it even harder to find a solution to avoid them all.

The use of superabsorbent polymers has been proven to be an interesting solution for the autogenous shrinkage problem and their applications can be wider, considering the self-healing and self-sealing of cracks. Still, one of the biggest challenges now is to find the one polymer or combination of polymers whose positive effects can overcome the loss in the mechanical strength. It has been shown in the results that high dosages of SAPs reduce considerably both the compressive and flexural strength of the cementitious materials. Despite of that, smaller amount of SAPs were found to be quite effective in the mitigation of the autogenous shrinkage.

In the future research the compositions presented will be used to assess the self-healing and self-sealing capacity of the SAPs. Further investigation will also be carried out on the influence of the SAPs on the internal relative humidity of the specimens and in the development of the capillary pressure.

4 Acknowledgements

The work has been financed by SIM program SHE (Engineered Self-Healing Materials) within the ICON project iSAP.

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